Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/EP05/002687

International filing date: 14 March 2005 (14.03.2005)

Document type: Certified copy of priority document

Document details:
Country/Office: DE
Number: 102004015182.2
Filing date: 25 March 2004 (25.03.2004)

Date of receipt at the International Bureau: 08 April 2005 (08.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)

PCT/EP2005/002687

BUNDESREPUBLIK DEUTSCHLAND

14.03.05

Prioritätsbescheinigung über die Einreichung einer Patentanmeldung

Aktenzeichen:	10 2004 015 182.2
Anmeldetag:	25. März 2004
Anmelder/Inhaber:	BASF Aktiengesellschaft, 67056 Ludwigshafen/DE
Bezeichnung:	Use of N-Methylcaprolactam
IPC:	C 07 D, B 01 D, C 11 D

Die angehefteten Stücke sind eine richtige und genaue Wiedergabe der ursprünglichen Unterlagen dieser Patentanmeldung.

München, den 17. Januar 2005
Deutsches Patent- und Markenamt
Der Präsident
Im Auftrag

Schäfer

A 9161
03/00
EDV-L

We claim:

1. The use of N-Methylcaprolactam as solvent, diluent, extractant, cleaning agent, degreaser, absorbent and/or dispersant.

2. The use of N-Methylcaprolactam as solvent and/or extractant in processes for fractionating gas mixtures.

3. The use of N-Methylcaprolactam as claimed in the preceding claim, the gas mixtures being obtained in cracking operations from hydrocarbons.

4. The use of N-Methylcaprolactam as claimed in either of the two preceding claims for the separation of acetylene, 1,3-butadiene and/or aromatics.

5. The use of N-Methylcaprolactam as solvent for polymers and/or copolymers.

6. The use of N-Methylcaprolactam as claimed in the preceding claim, wherein the polymers and/or copolymers are polymethyl methacrylates, polyesters, polyacrylonitrile, acrylonitrile copolymers, butadiene copolymers, styrene copolymers, N-vinylpyrrolidone copolymers, vinyl chloride copolymers, vinyl acetate copolymers, methyl methacrylate copolymers, terephthalic polyesters, polyvinyl chloride, polyvinylpyrrolidone, polyvinyl acetates, polycarbonates, polyethers, polyether sulfones, polystyrene, polyamides, polyimides and/or polyurethanes.

7. The use of N-Methylcaprolactam as solvent for resins, cellulose derivatives and dyes.

8. The use of N-Methylcaprolactam as solvent, diluent and/or dispersant in chemical reactions.

9. The use of N-Methylcaprolactam as claimed in the preceding claim, wherein the chemical reactions are C-C linking reactions and/or polymerizations.

10. The use of N-Methylcaprolactam as solvent in processes for producing wire enamels.

11. The use of N-Methylcaprolactam as solvent and/or absorbent in processes for gas scrubbing.

12. The use of N-Methylcaprolactam as claimed in the preceding claim for the separation of SO_2, H_2S and/or vinyl chloride.

13. The use of N-Methylcaprolactam as solvent, cleaning agent and/or degreaser in processes for producing integrated circuits (ICs).

14. The use of N-Methylcaprolactam as a partial or complete substitute for N-methyl-2-pyrrolidone (NMP), chlorinated hydrocarbons and/or ethers.

15. The use of N-Methylcaprolactam as claimed in any of claims 1 to 13 as a partial or complete substitute for N-methyl-2-pyrrolidone (NMP), chlorinated hydrocarbons and/or ethers.

16. The use of N-Methylcaprolactam as claimed in any of the preceding claims, wherein N-Methylcaprolactam is used in a purity of >99% by weight.

17. The use of N-Methylcaprolactam as claimed in any of the preceding claims, wherein N-Methylcaprolactam treated beforehand with an acidic cationic exchanger is used.

Use of N-Methylcaprolactam

Description

The present invention relates to uses of N-Methylcaprolactam (N-Methyl-epsilon-caprolactam, CAS No. 2556-73-2), especially in particular processes.

As a high-polarity, aprotic and broadly applicable organic solvent with low viscosity, which is homogeneously miscible with water and other organic solvents, N-methyl-pyrrolidone (NMP) is established in research and in industry.

By way of example, mention may be made here of the following publications relating to NMP:

W.C. Walsh, M. Waldrop and R. Atkins, "A process to Vacuum Vapor Degrease Metal Parts with N-Methyl Pyrrolidone", 1997, CA Abstract No. 127:7688.

The brochure "Formulating Paint Strippers with N-Methylpyrrolidone", BASF Corporation, Chemical Intermediates, 1990, USA,

and also the following 17 publications by BASF Corporation, Chemicals Division, USA:

W.C. Walsh, "Removal of Rosin and Resin based Solder Flux from electronic assemblies with N-methylpyrrolidone/water mixtures",

W.C. Walsh, "Degreasing and Solvent Regeneration in Metal Parts, Cleaning using N-Methylpyrrolidone", e.g.: http://es.epa.gov/p2pubs/oaic/301.html.

W.C. Walsh, "Surface Tension Modification of NMP-based Paint Strippers",

W.C. Walsh, "N-Methyl Pyrrolidone (NMP Technical Tips), Removal of Paints and Coatings from NMP Soluble Plastics",

Walsh, W.C. (1991), "Surface Tension Modification of NMP-based Paint Strippers". In: Reducing Risk in Paint Stripping, Washington D.C., 12-13 February 1991, pp. 177-184. Economics and Technology Division; Office of Toxic Substances; United States Environmental Protection Agency, Washington D.C. 1991,

W.C. Walsh, "N-Methyl Pyrrolidone (NMP Technical Tips), Maintenance Cleaning of Aircraft Ball Bearing Assemblies",

W.C. Walsh, "N-Methyl Pyrrolidone (NMP Technical Tips); Cleaning of a Chlorinated Paraffin/Metal Stearate Based Drawing Compound Off of 1000 Ft. Long Coils of 0.25 Inch, 316 Stainless Steel Tubing",

W.C. Walsh, "N-Methyl Pyrrolidone (NMP Technical Tips), Chemical Warfare Resistant Coatings (CARC), Removal From Metal Surfaces",

W.C. Walsh, W. Monahan and M. Waldrop, "Reflux Cleaning of Large Reactors with N-Methyl Pyrrolidone (NMP)",

W.C. Walsh, "Replacement of MEK with N-Methyl Pyrrolidone (NMP) in Coatings Plant Resin Clean Up Operations",

W.C. Walsh, "N-Methyl Pyrrolidone (NMP) Technical Tips, Removal of POLYURETHANE/POLYUREA RESIDUE from the Interior Surfaces of a Batch Reactor Vessel",

W.C. Walsh, "N-Methyl Pyrrolidone – Cleaning Applications in the Urethane Manufacturing and Processing Industries",

M.W. Waldrop and W.C. Walsh, "Modification of a Vapor Degreasing Machine for Immersion Cleaning using N-Methyl Pyrrolidone,

W.C. Walsh, "Removal of N-Methyl Pyrrolidone From Metal Parts Using A Centrifugal Dryer",

W.C. Walsh, M. Waldrop and R. Atkins, "A Process to Vacuum Vapor Degrease Metal Parts with N-Methyl Pyrrolidone", http://es.epa.gov/techpubs/3/15413.html,

W.C. Walsh, R.T. Chwalik, K.E. Hinzman and M. Waldrop, "Removal of N-Methyl Pyrrolidone (NMP) form Industrial Plant Exhaust Air with a Packed Column Scrubber", and

W.C. Walsh, "N-Methyl Pyrrolidone (NMP Technical Tips), Reclaiming or Recycling of NMP", and additionally

"Electrical Insulation – From Wire enamel to Enamelled Wire", 1 Beck Information, July 1992, (Beck Electrical Insulation Systems, Hamburg).

It is an object of the present invention to find a replacement for NMP and also chlorinated hydrocarbons and/or ethers which exhibits properties which at least

approximate to, preferably are as good as, and in particular are also improved, in the applications in which these substances, especially NMP, are employed.
This replacement for NMP ought also to exhibit similar physical properties, in relation for example to viscosity, colorlessness, polarity, inertness, biodegradability, homogeneous miscibility with other organic solvents and water. The replacement ought in particular to have even more favorable toxicological properties, i.e., to be even less toxic, than NMP.

We have found that this object is achieved by N-Methylcaprolactam, which is such a replacement for NMP and also chlorinated hydrocarbons and/or ethers.

The invention accordingly provides for the use of N-Methylcaprolactam as solvent, diluent, extractant, cleaning agent, degreaser, absorbent and/or dispersant.

N-Methylcaprolactam is a slowly evaporating (vapor pressure: 2.2 torr / 67 °C), highly polar, aprotic, general-purpose organic solvent (boiling point: 106-108 °C / 6 mm Hg) with favorable, ecological data (cf. safety data sheet on N-Methylcaprolactam from Sigma-Aldrich Chemie GmbH, Germany, Product No. 224766, 2/2004 – 4/2004).
It is a colorless, low viscosity liquid with a faint amine odor. N-Methylcaprolactam is fully miscible with water and most organic solvents.

Furthermore N-Methylcaprolactam has favorable toxicological data. (cf. safety data sheet on N-Methylcaprolactam from Sigma-Aldrich Chemie GmbH, Germany, Product No. 224766, 2/2004 – 4/2004).

In comparison with traditional solvents, N-Methylcaprolactam has some outstanding features:

Recyclable, non-corrosive, high flash point, high ignition temperature (218 °F, 103 °C), low surface tension, solves inorganic substances like inorganic salts, separates aromatic from aliphatic compounds and highly biodegradable.

Examples of such inorganic substances are: sulfur, zinc chloride, sodium nitrite, sodium bromide, mercury chloride, and certain iron salts, copper salts and lead salts.

All the above-mentioned features make N-Methylcaprolactam a good or the best choice for a wide range of different applications (see below).

N-Methylcaprolactam is the lactam of 5-methylaminocaproic acid and a very weak base. N-Methylcaprolactam is a chemically stable and powerful polar solvent. These characteristics are highly useful in a variety of chemical reactions where an inert medium is of concern:

Reaction Medium for Organic Synthesis

Compared to other solvents N-Methylcaprolactam often adds desirable catalytic effects and gives better conversions when used as a solvent in chemical reactions. This advantageous property is of great importance.

Alkylation on Acetylides

The preparation of acetylides under mild conditions is successful in N-Methylcaprolactam, whereas these products in general require alkylation of acetylenes in liquefied ammonia [Compare for example: GE 944 311 (BASF, 1956)].

Reppe conditions

N-Methylcaprolactam is also advantageous as reaction medium offering improved processing course for the ethynylation and vinylation under Reppe-conditions [Compare for example: W. Chodkiewicz, Ann. de Chim. (Paris), 2 (13), 819 (1957); GE 940 981 (BASF, 1956)].

Synthesis of Nitriles

The use of N-Methylcaprolactam as a solvent in the Rosemund von Braun nitrile synthesis enhances yield and shortens the reaction time, furthermore it dissolves all reactants to a homogeneous liquid phase [Compare for example: M.S. Newman and D.K. Philipps, J. Am. Chem. Soc. 81, 3667 (1959)].

Reactions of Synthesis Gas in N-Methylcaprolactam

Carboxylic acids, anhydrides and esters can be prepared by reaction of alcohols with synthesis gas ($CO + H_2$) using nickel or cobalt complexes in N-Methylcaprolactam. Another method is the preparation of ethylene glycol from synthesis gas. The combination of a rhodium carbonyl species and N-Methylcaprolactam forms a solution with excellent activity and selectivity for ethylene glycol formation [Compare for example: E. Watanabe et al., J. Chem. Soc., Chem. Commun. (3), 227 (1986)].

Despite the stability of N-Methylcaprolactam, it can also play an active role in certain reactions: hydrolysis, oxidation, condensation, conversion with chlorinating agents, polymerization and o-alkylation, and related reactions.

N-Methylcaprolactam preferably also finds inventive use in the following known processes, in which it replaces NMP (see, for example, the BASF AG brochure “BASF Intermediates”, “N-Methylpyrrolidone (NMP)”, No. CZ 3307 e-0291-2.0 (around 1994) and the literature cited therein, which is hereby expressly incorporated by reference):

A) Recovery of pure hydrocarbons in petrochemical processing

An application for N-Methylcaprolactam is the recovery of hydrocarbons by extractive distillation. This technique utilizes the high solubility of hydrocarbons in N-Methylcaprolactam and the fact that differences in volatility are sometimes considerably increased in the presence of N-Methylcaprolactam. Compared to other commercial solvents and extraction media, N-Methylcaprolactam offers the following advantages: no azeotropes are formed with hydrocarbons; N-Methylcaprolactam is very resistant to heat and chemicals; and N-Methylcaprolactam has a favorable toxicological and environmental profile.

N-Methylcaprolactam is miscible with water in all proportions. This allows setting the process to the desired conditions and stripping the dissolved hydrocarbons from the solvent. N-Methylcaprolactam has a high boiling point corresponding with low vapor pressure, keeping losses in commercial-scale separation processes to a minimum. The viscosity is low at the temperatures typically encountered in practice, which favors mass transfer.

Acetylene

N-Methylcaprolactam may successfully be used for the removal and purification of acetylene from mixtures of cracked gases obtained in the partial combustion of saturated hydrocarbons [Compare for example: H. Höfermann et al., Chem. Industrie 21, 860 (1969) ; H. Friz, Chem.-Ing.-Techn. 40 (20), 999 (1968)]. 8 to 10 % of the gas volume obtained by this pyrolysis reaction consist of acetylene, about 4 % of carbon dioxide, hydrogen and carbon monoxide. At ambient conditions N-Methylcaprolactam dissolves many times its own volume of acetylene. Acetylene can be easily separated from the light key component carbon dioxide, as well as from higher acetylenes. A special advantage of this process is that there is no risk for the acetylene to decompose spontaneously.
Natural gas, naphtha or liquefied petroleum gas (LPG) are converted to an acetylenic gas in the BASF submerged flame process [Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., VCH Verlagsgesellschaft, Weinheim, Vol. A1, 107 (1985)] using a water quench and coke deposit removal or using an oil quench which coke deposit removal and recovery of heat. The purification of the cracked gas received consists of two stripping steps, where N-Methylcaprolactam may be used as a selective solvent.

1,3-Butadiene

A C_4-fraction is obtained in large amounts as a by-product in the manufacture of ethylene by the steam cracking process and similar commercial-scale pyrolysis

reactions. The butadiene content of these fractions is typically around 40 to 50 g / 100 g.

N-Methylcaprolactam is highly effective for separating butadiene from butene or from C4-acetylenes due to its excellent selectivity. In the BASF butadiene process [U. Wagner and H.M. Weitz, Ind. Eng. Chem. 62, 43 (1970); B. Hausdörfer, U. Wagner and H.M. Weitz, Chem.-Ing.-Techn. 40 (23), 1147 (1968); K. Volkamer et al., Erdöl, Kohle, Erdgas, Petrochem. 34 (8), 343 (1981)] N-Methylcaprolactam containing for example 5 to 10 g/100 g water may be used in a two stage countercurrent gas scrubbing. Butadiene of either SBR (Styrene Butadiene Rubber) or poly-cis quality is obtained. The concentration of N-Methylcaprolactam in the resulting pure butadiene does not exceed 10 mg/kg (ppm). The same procedure may also be used for separating C_4-olefins and C_4-paraffins.

In the BASF extractive distillation procedure [Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., VCH Verlagsgesellschaft, Weinheim, Vol. A4, 437 (1985); B. Linnhoff and W. Lenz, Chem.-Ing.-Techn. 59 (11), 851 (1987); CA Abstract No. 140:78725, 2004; CA Abstract No. 138:402099, 2003] a butadiene is obtained from C_4-hydrocarbon feedstocks in high purity (99,5 to 99,9 g/100 g) and high yields (98 %). As the essential process step N-Methylcaprolactam may be used as a selective solvent containing for example approximately 8 g / 100 g of water in a, e.g. two stage, extractive distillation.

Isoprene

The BASF method of recovering isoprene (2-methyl-1,3-butadiene) is a development of the butadiene process described above. Either extractive distillation or liquid-liquid extraction may be employed for the separation. As a rule, C_5-Cuts from pyrolysis reactions contain 15 to 20 g/100 g of isoprene. The purity of the end product is high, e.g. 99 % [H. Kröper and H. M. Weitz, Oil Gas J. 65 (2), 98 (1967)].

Aromatics

By the LURGI Arosolvan process, aromatics can be extracted from mixtures of hydrocarbons, like reformed or hydrogenated pyrolysis gasolines [K. Eisenlohr, Erdöl und Kohle 16, 523 (1963); E. Müller and G. Höhfeld, Erdöl und Kohle 24, 573 (1971); E. Müller, Chemiker Zeitung 95, 996 (1971); E. Müller, Chem. and Industry 11, 518-22 (1973); E. Müller, VT Verfahrenstechnik 8 (3), 88 (1974)]. A high yield of benzene, toluene, xylene, and other aromatics with boiling points below 180°C is obtained. Additives to the N-Methylcaprolactam are chosen to ensure a solvent blend of optimum selectivity and high solvent capacity. The latter term is defined as the ratio of the aromatics concentration in the solvent phase to that in the hydrocarbon phase. An advantage of N-Methylcaprolactam over other solvents is that conditions are optimal for distillative separation of the extracted aromatics due to the favorable

location of its boiling point. Another benefit is that the phases can be separated quite rapidly utilizing the difference in density; and yet another is that N-Methylcaprolactam is chemically and thermally stable at the temperatures employed in the process. In the Distapex process of LURGI GmbH, pure benzene is extracted from the crude product by extractive distillation using NMP as the selective solvent, which can be substituted by N-Methylcaprolactam. The same applies to toluene and xylene respectively from the corresponding distillation phases. This process is particularly advantageous if the crude products are already available as separate B-, T- or X-cuts and the concentration of the aromatic compounds exceeds 70 % [I.B. Lane et al., Chem. Process Engng. 48 (1), 49 (1967); E. Müller, VT Verfahrenstechnik 14, 551 (1980)]. Mixtures of monocyclic and polycyclic alkyl-substituted or unsubstituted aromatics can also be separated with a blend of N-Methylcaprolactam and water [compare: Ohio Oil, US 2 943 122 (1960)]. Likewise aromatic hydrocarbons can be removed from naphtha and kerosene with a boiling range of 30 to 300°C by selective extraction with N-Methylcaprolactam and reextraction with a cosolvent [compare: Metallgesellschaft, EP-A-87 832 (1983)].

B) Desulfurization of gases and removal of acidic compounds in gases

High concentrations of acidic compounds are often present in natural or synthesis gases. Examples are hydrogen sulfide, carbon oxysulfide, carbon dioxide and organic sulfur compounds. Rather than applying a chemical process, they may be removed by physical scrubbing in several stages with a mixture of N-Methylcaprolactam, alcohol and water [compare: Metallgesellschaft, GB 938 392 (1963) and DE 2 250 169 (1974); EP-A-13177; CA Abstract No. 82:60774, 1984; CA Abstract No. 76:61312, 1984].

The difference between the Bunsen solubility coefficient for hydrogen sulfide and that for carbon dioxide is large enough that these gases can be easily separated and recovered in a pure form [compare: G. Hochgesand, Ind. Eng. Chem. 62 (7), 32 (1970)].

C) Lubricating Oils

High performance lubricating oils are a blend of petroleum fractions from which quality-impairing aromatics, nitrogen-, oxygen- or sulfur-compounds have been extracted by solvent refining. Afterwards the components with the best lubrication properties - the isoparaffins - are separated from the N-paraffins.

The aromatics and other impurities dissolve to different extents in organic high boilers. These differences are utilized in removing them from the paraffins in industrial solvent refining. An advantageous solvent for this purpose is N-Methylcaprolactam [compare: J. D. Bushnell and R. T. Fiocco, Hydrocarbon Proc. 59 (5), 119 (1980); A. Sequeira, P.B. Sherman, T.U. Donciere, and E.O. McBride, Hydrocarbon Proc. 58 (9), 155 (1979)].
The refining process consists of admitting the feedstock to the bottom of the extraction column and allowing it to flow countercurrent to the degassed N-Methylcaprolactam. Thus the column is designed as a multistage extraction zone. As a result of the equilibria established in all stages, a refined product containing the paraffins is withdrawn overhead. The extract containing the more soluble components, i.e. the aromatics and other impurities, is withdrawn at the bottom of the column. Both streams, the refined product and the extract, must subsequently be distilled at an elevated temperature or reduced pressure in order to remove the N-Methylcaprolactam. Eventually three segments will have been separated: the almost N-Methylcaprolactam-free paraffins, the extracted impurities, and N-Methylcaprolactam which in turn can be recycled to the head of the extractor.

N-Methylcaprolactam is much superior to furfural and phenol for the lube oil extraction process [compare: A. Sequeira et al., Hydrocarbon Proc. 58 (9), 155 (1979)].

Some advantages of N-Methylcaprolactam over other solvents are for example: N-Methylcaprolactam is thermally and chemically stable, has favorable toxicological and ecological properties, has an excellent selectivity and is a very good solvent in terms of raffinate yields.

D) Plastics

N-Methylcaprolactam may be used as a solvent for natural and synthesis plastics, waxes, resins and various types of paints. It dissolves polymers, such as cellulose derivatives, polymethyl methacrylate, polyamides, polyimides, polyesters, polystyrene, polyacrylonitrile, polyvinyl chloride, polyvinyl pyrrolidone, polyvinyl acetate, polyurethanes, polycarbonates, polyethersulfones, polysulfones, polyethers and many copolymers.

N-Methylcaprolactam is miscible with the corresponding monomers and with conventional organic solvents and water. As a result, the best possible solvent blend for a given application can be found.

The following examples illustrate the advantages of N-Methylcaprolactam showing options for solving problems, which may arise in the plastic industry.

Moldings

The production of fibers, films, tapes, etc. from linear high polymers frequently presents technological problems. The difficulty is, that there is a lack of solvents or plasticizers, that are noncorrosive, physiologically harmless and non-flammable at the processing temperature. N-Methylcaprolactam is very useful in cases of this nature, because it allows highly concentrated solutions or moldable compounds to be produced from polyamides, polyacrylonitrile, polyvinyl chloride, polystyrene, and cellulose triacetate. The same applies at elevated temperature to vinyl fluoride homopolymers and copolymers.
By virtue of its swelling and solubilizing action, N-Methylcaprolactam can also be used for cold-welding of plastics.

Synthetic Fibers

Aromatic polyamides are excellent components for the production of films, fibers and yarns, which offer the extremely high strength needed in engineering applications. Poly(p-phenylene terephthalamide), which is preferred by industry as a starting material, can be synthesized by reaction of p-phenylene diamine and terephthaloyl dichloride in concentrated N-Methylcaprolactam solvent systems. High performance aramid fibers and yarns can be produced by spinning solutions of poly(p-phenylene terephthalamide) or other polymer compositions an polyamide-basis employing conventional wet-and dry-spinning techniques.

N-Methylcaprolactam containing lithium chloride is a solvent for the manufacture of polymers made from aromatic diamines and aromatic acid chlorides, such as isophthaloyl chloride, that can form fibers and coatings and that are stable to high temperatures.
Polyacrylonitrile, which is insoluble in most organic solvents, can be dissolved in N-Methylcaprolactam containing small amounts of lower aliphatic ketones. These solutions can be spun at comparatively low temperatures to uniform fibers.
Fibrous block poly(arylene ether sulfone) - poly(arylene terephthalate) copolymers may be prepared using a solution of potassium carbonate and N-Methylcaprolactam and interfacial methods.
Fibers of poly(arylacetylene) may be wet-spun in organic solvents like N-Methylcaprolactam.
Urea can be condensed with diamines in N-Methylcaprolactam at temperatures above 150°C. The linear, uncrosslinked polyureas thus obtained have high molecular weight and good mechanical properties and can be processed to fibers. N-

Methylcaprolactam dissolves both the polymers and the monomers at elevated temperatures, but the polymers are precipitated when the solution is cooled to room temperature. Thus N-Methylcaprolactam is superior to a phenolic solvent because it simplifies the process and improves the quality.
In the synthesis of polyureas with a high melting point from aromatic diamines and aromatic diisocyanates, a suitable non-corrosive, inert solvent for the condensation reaction and subsequent spinning is N-Methylcaprolactam.
Mixtures of polyacrylonitrile with formylated polyvinyl alcohol dissolved in N-Methylcaprolactam and of polyacrylonitrile with poly(alkyl-alpha-acylaminoacrylates) are stable; they do not separate and can be spun to homogeneous, non-segmenting fibers with a high softening point and good affinity for dyes.
N-Methylcaprolactam and its blends with tetrahydrofuran or phenol are suitable for producing spinning solutions of vinyl chloride polymers, vinylidene chloride polymers, and synthetic linearly condensed polyesters derived from polyethylene terephthalates. The solutions obtained are stable, do not gel, and have a low viscosity at a high solids content. They allow the production by wet or dry techniques of fibers, films, with superior physical properties for the manufacture of textiles.

Membranes

N-Methylcaprolactam may be used for the preparation of semipermeable membranes. These membranes are employed in separation processes like ultrafiltration and reverse osmosis.

Polyether sulfone membranes can be prepared from multicomponent systems of N-Methylcaprolactam, water and respective polymers [compare: G. Tkacik and L. Zeman, J. Membr. Sci. 31 (2-3), 273 (1987)].

Polysulfone membrane properties are influenced by solutions in N-Methylcaprolactam and dimethylsulfoxide and calcium chloride as pore-forming agent.
In the preparation of reinforced polysulfone membranes blends of N-Methyl-caprolactam and polyethylene glycols may be used as swelling agents [compare: X. Lu, C. Gao, and X. Sun, Chem. Abstr. 104 (24) 208436v (1985)].

Synthesis of Polymers

N-Methylcaprolactam allows the synthesis of new polymers and/or the synthesis of polymers with an improvement in their quality.

In the manufacture of polyurethane foams, N-Methylcaprolactam catalyzes the foaming reaction to produce highly hydrophilic, soft articles. In foamed polyether urethanes, N-Methylcaprolactam acts as a regulator to ensure open cellular

structures. Polyester urethane rubber solution properties in the presence of N-Methylcaprolactam are advantageous.

Linear synthetic polyamides are readily soluble in N-Methylcaprolactam at 150 to 200°C and sparingly soluble at room temperature; the same applies to polycaprolactam and copolymers of caprolactam with, for example, N-vinyl caprolactam. This property allows to remove impurities, such as unconverted monomers and colored substances by recrystallization.

Polycondensation reactions involving aminocarboxylic acids and their lactams or salts of polycarboxylic acids and polyamides can be done in phenol. If this solvent is replaced by N-Methylcaprolactam fibers or moldings of superior quality are obtained, and simplifications are achieved in the production process.

When linear, high-viscosity polyamides are produced from ß-lactams, solvents such as N-Methylcaprolactam are very suitable. N-Methylcaprolactam dissolves the monomer and the activator and swells the polymer as it is being precipitated.

If acrylates or methacrylates are polymerized anionically in the presence of dipolar, aprotic cocatalysts, such as N-Methylcaprolactam, the proportion of syndiotactic polymer will increase, with the consequence that the products obtained will have a more regular structure. The resulting improvements in resistance to deformation by heat, resistance to solvents, and mechanical properties make these products suitable molding compounds and binders for surface coatings.

Handling at room temperature of the well-known curing agent for epoxyether resins, m-phenylene diamine is much easier and less dangerous when it is dissolved in N-Methylcaprolactam. This solution lengthens the potlife of the resin and does not exert an adverse effect on the curing characteristic. A melt that has solidified at low temperatures becomes a homogeneous liquid again on thawing.

Photocuring of acrylic epoxy resins is possible using N-vinylpyrrolidone as a reactive and N-Methylcaprolactam as a non-reactive diluent.

Amorphous polyacrylethers, which are highly stable to temperatures, can advantageously be prepared using N-Methylcaprolactam. The use of weak bases prevents side reactions [compare: D. K. Mohanty et al., Polymer Preprints 25 (2), 19 (1984)].

N-Methylcaprolactam may be used as the reaction medium in the synthesis of high performance poly(phenylene sulfide) for the polymerization of p-dichlorobenzene and sodium sulfide.

Ring opening polymerization of poly(aminobenzoyl lactams) is possible in the solvent system N-Methylcaprolactam and lithium chloride.

E) Surface Coatings

N-Methylcaprolactam is a non-corrosive high boiler with excellent solvent power and chemical resistance. Thus, N-Methylcaprolactam improves the properties of many surface coating systems. In particular, these effects are favorable for baked coatings that are cured at relatively high temperatures. N-Methylcaprolactam allows the production of highly filled paints and finishes. Since it improves the rheological properties, paints with superior flow-out and covering power are obtained. Hence, the coatings are more homogeneous, non-porous and non-cratering, and they display greater resistance to chemicals and higher mechanical strength.

N-Methylcaprolactam is an excellent solvent for most coating raw materials, such as acrylate, epoxy resins, polyurethanes, polyvinyl chloride systems, polyamideimide based wire enamels, waterbased coatings and printing inks, e.g. ink jet inks, such as waterfast ink jet inks optionally containing a UV curable resin.

N-Methylcaprolactam is a useful solvent for butadiene acrylonitrile copolymers (e.g. Perbunan N), which are used for the lining of tanks. The rubber solutions have better flow and leveling than those obtained with ketones.

Vinylchloride-vinylacetate-copolymers may be dissolved in a blend of N-Methyl-caprolactam and mononuclear aromatic hydrocarbons to give a solution which can be used for film-casting. As a result of the synergistic effect between the two solvents, the solutions have a low viscosity and can be applied readily.

Polyisocyanates which contain imide groups can be dissolved in solvent systems with N-Methylcaprolactam. These solutions can be used for rubberizing compounds and metal surfaces.

Wire Enamels

An important feature of N-Methylcaprolactam in the manufacture of thermosetting paints for electrical insulation is its excellent solvent power for polycarboxylic acids and their anhydrides, such as trimellitic and pyromellitic anhydrides, and polymers with amide and carboxyl groups with a high aromatic content.
Thus polyisocyanates containing amide groups are formed in the condensation reaction between N-Methylcaprolactam solutions of polybasic carboxylic anhydrides

and monomeric polyvalent isocyanates. The baking finishes obtained yield coatings with outstanding mechanical and dielectric properties an copper conductors. From the technical point of view N-Methylcaprolactam offers the advantage of performing a double function: It serves as a reaction medium in the manufacturing process, remaining in the final coating, as a viscosity modifier.

N-Methylcaprolactam is a suitable solvent for the resinous copolyesters in the reaction between a diimide (like that obtained from trimellitic anhydride and 4,4'-diaminodiphenylmethane) and polyhydric alcohols (like trishydroxyethylisocyanurate (THEIC) or ethylene glycol). The solutions thus formed can be baked to yield highly heat-resistant wire enamels. N-Methylcaprolactam is also a solvent for polyamide/polyimide baking finishes derived from the condensation of a tricarboxylic acid aromatic and aliphatic diamines.

Solvent blends of N-Methylcaprolactam and dicarboxylic acid esters are useful in the production of wire enamels on the basis of polyvinyl formal.

F) Paint Stripping and Cleaning

Due to its high solvating power for plastics, resins, oil and grease, N-Methylcaprolactam can successfully be employed as an ingredient in paint removers, cleaners and degreasers. Its miscibility with water and most conventional organic solvents allows the manufacture of highly effective products, which can be tailor made for use in different applications. The environmental and toxicological data of N-Methylcaprolactam are favorable compared to most other solvents. N-Methylcaprolactam is not corrosive. Blends containing N-Methylcaprolactam and other solvents often show desirable synergistic effects.

N-Methylcaprolactam can be used alone (pure) or in blends for removal of oil, carbon deposits and other tarry polymeric residues from metal chambers, pistons and cylinders, as well as for wet cleaning of combustion engines.

N-Methylcaprolactam may be part of blends used by the industry to clean soiled metal parts and equipment. Certain difficult-to-dissolve polyurethanes are best cleaned up using blends of N-Methylcaprolactam with dicarboxylic acid esters. Blends of N-Methylcaprolactam with other organic solvents and auxiliaries are utilized for removing printing ink residues.
Blends containing N-Methylcaprolactam as a key ingredient remove epoxies and similar chemically resistant coatings from steel surfaces as well as temporary coatings from optical instrument parts.

Solvent blends containing N-Methylcaprolactam as a reactive ingredient are suitable for production of a foam-type coating remover, which is useful for removing various paints, varnishes, lacquers, and other coatings or finishes, particularly from relatively large surfaces.

N-Methylcaprolactam can be used for the formulation of paint removers which are easy to handle, ecofriendly and reduce fire hazards.

Blends of N-Methylcaprolactam may be used for the cleaning of articles or surfaces soiled by such materials as oil, fat, soot, paint, and glue by immersion into a bath. An important field of application in this connection is the degreasing of metals before further surface treatment, coating or galvanizing. Cleaner baths to be used contain N-Methylcaprolactam, odor masking agents, surfactants, and diluents. By using a water absorption preventing layer, a considerable retardation of the water absorption of the cleaner is achieved.
Products based on N-Methylcaprolactam are applicable to the removal of weathered dispersion coatings on outdoor walls, for refurbishing interiors, for graffiti removal, and for ultrasonic cleaning of items such as optical lenses or dental prostheses.

The following solvents can be utilized to develop in combination with surfactants, thickeners, and other additives, systems of high solvent- and swelling power:

butanol, butylacetate, butylglycol acetate (1-butoxy-ethylacetate), gamma-butyrolactone, 2-ethyl-hexylacetate, 1-methoxy-2-propylacetate, nonanol, pentylacetate, Solvenon PM (1-methyl-2-propanol) and tridecanol.

G) Plant Protection

N-Methylcaprolactam can be used as a solvent or co-solvent for the formulation of insecticides, fungicides, herbicides, seed treatment products and bioregulators where highly polar compounds are required. N-Methylcaprolactam is given preference over other highly polar solvents because it is exempt from the requirement of a tolerance when used as a solvent or co-solvent in pesticide formulations applied to growing crops, and it possesses a favorable toxicological and environmental profile. It is especially useful in multicomponent systems.

N-Methylcaprolactam forms adducts with bacteriostats, such as substituted ureas, carbanilides, thiocarbamates, guanidines, salicylanilides. These products are more bactericidal and allow better growth control of bacterial cultures.

H) Electronic Equipment Manufacture

The production of integrated circuits (ICs) calls for products of very high purity. Electronic Grade N-Methylcaprolactam, is particularly manufactured by the processes according to EP-A1-1 038 867 (BASF AG) or US-A-5,777,131 (BASF Corp.). This makes N-Methylcaprolactam an excellent solvent for the electronic industry and producers of printed circuit boards. Blends of N-Methylcaprolactam with common solvents may be utilized for the cleaning and degreasing of single-crystal silicon wafers for ICs.

Using N-Methylcaprolactam as a dilutant in polyamideimide, urethane, and epoxy resins a smooth surface is obtained. The low evaporation rate of N-Methylcaprolactam allows the formation of very homogeneous coatings.

In micro-photolithography (key for the production of electronic chips) N-Methyl-caprolactam shows excellent performance in developers for light-curable polyimides and in photoresist strippers.

In their final production stage ICs are encapsulated with resins, such as epoxy molds. This process leaves flash or resin bleed on the IC package or the leadframe as well as on the encapsulation device. A finishing step may be performed by softening the resin with N-Methylcaprolactam, which then allows an easy removal by blasting with compressed air or high pressure water (chemical deflashing). It is recommended to perform this process immediately after molding and before postcuring.

Semiconductors and other electrical devices are soldered to printed circuit boards. This technique requires the use of a fluxing agent. Residues of flux have to be removed after the soldering process to prevent corrosion. This may be done with solvent-blends containing N-Methylcaprolactam as a key ingredient.

Another field of use is the selective removal of polymer coats from certain areas on printed circuit boards.

I)

N-Methylcaprolactam or its blends may be widely used as absorption media for the removal or separation of organic compounds from waste or flue gases, such as sulfur dioxide, hydrogen sulfide and vinyl chloride.

During processing of adhesives containing organic solvents part of these solvents may be replaced by N-Methylcaprolactam in order to reduce the concentration of vapors. PVC or ABS glues, which mainly consist of N-Methylcaprolactam and/or gamma-

butyrolactone, show reduced fire hazards. As both products have a relatively low vapour pressure, inhalation risk is considerably lowered.

J)

Inks and Pigments

For inks with azo compounds it is possible to prepare diazotizable amine dispersions with N-Methylcaprolactam, which dissolves the diazo components and coupling components. In order to improve the formation and durability of shades it is possible to use N-Methylcaprolactam when coloring polyamide, acrylic, and polyester fibers, fabrics, and films and when coloring polyester/cotton blends. In inks, including lithographic inks, and other protective or decorative pigment coatings, N-Methylcaprolactam effectively disperses many organic or inorganic color pigments without raising the water sensitivity of the film. 1% of solvent (based on pigment) facilitates grinding and increases the coloring strength, as a result of the refinement of the pigment. N-Methylcaprolactam improves the stability toward aging, results in reduced color drift, and stabilizes the system against flocculation and solidification.

K)

N-Methylcaprolactam may also be used

as a solvent for developer (Photo-/Reproduction-Technique),

for the manufacture of High Performance Adhesives and Industrial Adhesive Removers,

as a solvent for Slimicides used in the Manufacture of Paper and Paperboard,

as reaction medium or solvent in the synthesis of organic intermediates and pharmaceuticals,

as a solvent for coal extraction and in oil refining,

as a component in fluids for the preparation of printing plates,

for removing contaminations and adhesives, especially cyanoacrylate-based adhesives, from polymers, plastic (e.g. polymethacrylates), glass, metal, ceramic, stone and fiber surfaces and also from skin.

L)

N-Methylcaprolactam finds use as an NMP replacement in accordance with the invention in particular also in the processes and operations cited at the outset with respect to NMP.

M)

N-Methylcaprolactam is able successfully and advantageously to replace: dimethylformamide (DMF), especially in aqueous coatings, methylene chloride, especially in the stripping of memory chips, perchloroethylene and trichloroethylene, especially in vapor degreasing processes, chlorine-containing solvents (e.g., chlorinated hydrocarbons, especially chlorinated C1-C6 hydrocarbons, such as tetrachloroethylene and trichloroethylene) e.g. in ultrasound cleaning processes, sodium hydroxide in the cleaning of reactors to remove residues of urethane, for example, furfural phenol in lubricant extractions, and glycol ethers, for example in household and industrial cleaners and coatings, ethers such as THF, diethylene glycol dialkyl ethers, 1,2-diethoxyethane and 1,2-dimethoxyethane, for example, in chemical reactions, for example.

For the uses in accordance with the invention N-Methylcaprolactam is employed in particular with a purity of more than 97% by weight, in particular of more than 98% by weight, very particularly of more than 99% by weight, e.g., more than 99.8% or more than 99.9% by weight. These purities can be obtained by single or multiple distillation or rectification.

N-Methylcaprolactam with high purity for use in accordance with the invention is obtained in particular with the processes according to EP-A-1 038 867 (BASF AG) and US-A-5,777,131 (BASF Corp.) (see below).

The preparation and purification of N-Methylcaprolactam is known:

The preparation of N-Methylcaprolactam can take place by reaction of epsilon-caprolactone with monomethylamine at elevated temperature and superatmospheric pressure, releasing one mole equivalent of water, e.g. in analogy to Ullmann's Encyclopedia of Industrial Chemistry, Vol. A22, 5th Ed., page 459 (1993).

The preparation of N-Methylcaprolactam can take also place by methylation of epsilon-caprolactam, e.g. with methanol; see for example Chem. Abstract No. 120:191559 (RO-B1-102421) and Chem. Abstract No. 118:233904 (EP-A1-531 673) and DD-A1-267 729

EP-A1-1 038 867 (BASF AG) and US-A-5,777,131 (BASF Corp.) describe processes for purifying N-substituted lactams such as NMP and N-Methylcaprolactam, the impure N-substituted lactams being treated with an acidic, in particular macroporous, cation exchanger.

Use of N-Methylcaprolactam

Abstract

Use of N-Methylcaprolactam as solvent, diluent, extractant, cleaning agent, degreaser, absorbent and/or dispersant, in particular as partial or complete replacement for N-methyl-2-pyrrolidone (NMP), chlorinated hydrocarbons and/or ethers.